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XII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE. — J. P. Cooke, *Director*.

ADDITIONAL NOTE ON THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.

By Josiah Parsons Cooke and Theodore William Richards.

Presented March 14, 1888.

The preceding paper on this subject was already in print, and a number of the extra copies had been distributed, when the writer received a letter from Lord Rayleigh stating that he had been engaged on a similar work, and had observed that the glass balloon used in Regnault's method of weighing gas volumes, when exhausted, was sensibly condensed by the pressure of the air. Obviously, if this were true, the *tare* of the balloon thus exhausted would be too large in consequence of the lessened buoyancy of the atmosphere, and hence the subsequently observed weight of gas when the balloon was filled would be too small. A shrinkage amounting to a single cubic centimeter would make a difference of about 1.29 milligrams, and Lord Rayleigh suggested that our results might have been influenced by a constant error arising from this source. As the same balloon represented in Figure 1 of the preceding paper had been used in all our determinations, and was still in good condition, there was no difficulty in determining the amount of shrinkage under exhaustion, and thus finding the correction which ought to be applied to the results on this account. The method we used was briefly as follows.

The balloon was first exhausted, and then completely filled with boiled distilled water at an observed temperature. The weight of this water having been taken, and the internal volume of the balloon thus determined, a small portion of the water — 190 cubic centimeters — was run out, and the volume estimated both by direct measurement and also by reweighing the balloon. With these data we could readily calculate the volume of air left in the balloon for any given temperature, and the small amount of water lost by evaporation in the subsequent exhaustion produced no sensible effect on the result, as a knowledge of the volume within five cubic centimeters was all that the present problem required, and the water did not lose in weight more than two grams during the whole series of experiments.

The balloon was now thoroughly exhausted, allowed to stand, and again exhausted several times, until a vacuum gauge connected with it remained constant over night, and indicated the calculated tension of aqueous vapor, which showed that all the air — dissolved or otherwise — had been practically removed.

A sufficient mass of water was left in the balloon to sink it under water, and thus immersed in a large vessel filled with distilled water, (which had been boiled and allowed to cool,) it was now suspended from the beam of the balance used throughout this investigation. No air bubbles formed on the glass, and care was taken to remove all entangled air from the connecting tubes. The weight soon became constant, and the tare could be accurately determined within a centigram. The connecting tubes of the balloon were next lifted above the surface of the water, and, after carefully drying the inlet, the outside air was admitted, and the temperature of the water in the tank and the height of the barometer observed. On again immersing the balloon there was a large loss of weight, — about 1.4 grams, — over six times the weight of air admitted, — only about 0.2 gram. There had evidently been a marked shrinkage under exhaustion amounting to about 1.6 cubic centimeters. This decrease of weight was noted after the equilibrium had become constant, usually in about five minutes.

It is probable that the admitted air was saturated with moisture, and the calculation is based upon that assumption; but this would make no practical difference in the weight so far as the problem before us is concerned. Appended is an example of the method.

SERIES I. *Determination* 2.

Tare of globe exhausted = 198.22 grm. T° = 17°.30.
" " filled = 196.83 " T° = 17°.30.
Observed loss of weight = 1.39 "

Atmospheric pressure = 75.86 c. m.
Tension of aqueous vapor = 1.46 "
Difference = 74.40 "

Weight of 188 c. c. moist air at 17°.3 and 74.4 cm. = .22 grm.
Observed loss of weight of globe = 1.39 "
Water displaced by difference of volume = 1.61 "

Diff. of volume corresponding to 74.4 cm. pressure = 1.61 c. c.
" " " 76.8 cm.* " = 1.66 c. c.

Weight of 1.66 c. c. of air at 76 cm. and 22° C.* = 1.98 mg.

Below are given the data of the two series of determinations which were made.

Series I.

Number.	Loss of Weight. Grams.	Atmospheric Pressure. Centimeters.	Temperature. °C.	Correction. Milligrams.
1.	1.34	76.40	18.10	1.92
2.	1.39	75.86	17.30	1.98
3.	1.39	75.80	17.32	1.98
4.	1.37	75.78	17.40	1.96
5.	1.39	75.75	17.45	1.99
				1.97

Series II.

Number.	Loss of Weight. Grams.	Atmospheric Pressure. Centimeters.	Temperature. °C.	Correction. Milligrams.
6.	1.38	75.60	14.50	1.98
7.	1.39	75.60	14.50	2.00
8.	1.39	75.58	14.60	1.99
9.	1.40	75.58	14.61	2.01
10.	1.39	75.58	14.65	1.99
				1.99

Total average, 1.98 milligrams.

The quantity 1.98 milligrams is then the correction sought, and this closely agrees with Lord Rayleigh's estimate of the value in the letter above referred to. Since in the work described in the preceding paper all the data required for the calculation were not recorded in every case, it will be impossible to apply this correction to each determination separately. But no sensible error can result if we add the correction to the average apparent weight of the hydrogen, easily calculated from the data given in the table on page 173.

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* 22°C. and 76 cm. pressure were the average atmospheric conditions at the times of weighing the globe in the previous determinations, and 76.8 cm. was the average difference of the pressure on the globe when exhausted and full of hydrogen.

The total weight of the hydrogen burnt in the sixteen determinations as observed was 6.7029 grams. Add to this sixteen times the correction, or $16 \times 0.00198 = 0.0317$, and we obtain 6.7346 grams for the corrected weight. The total weight of the water formed was 60.1687 grams. Hence we find by difference for the total weight of oxygen consumed in the combustions 53.4341 grams; and the corrected atomic weight of oxygen is $2(53.4341 \div 6.7346) = 15.869$.

The probable error of this result is no greater than that of the "Total average" given on page 173; for the value of the constant correction must be certainly known within the one fiftieth of a milligram. It is true that there are several variable elements which enter into the determination of this value, but they can all be estimated with far greater accuracy than the conditions of our problem require. We may therefore write as the present result of our work, $H : O = 1.000 : 15.869$.

Atomic weight of oxygen, **15.869 ± 0.0017.**

If we compare this result with that of Dumas, as before, on page 175, we have for the complete analysis of water, —

Percentage of oxygen after Dumas	88.864 ± 0.0044
Percentage of hydrogen after final result . .	11.193 ± 0.0011
	100.057

It would now appear that the close agreement before shown was a mere coincidence, and that there must have been a small constant error either in our own process or in that of Dumas. Where the error lies further investigation can alone determine; for although, after a careful revision of our work, we can discover no flaw, no one can be confident that such a constant error as has already appeared may not hereafter be found, — and certainty can only be secured after repeated confirmations by essentially different methods. While, therefore, we feel bound to acknowledge without delay the cause of constant error which Lord Rayleigh has pointed out, we give our corrected result as subject to further revision. It has been suggested by Lord Rayleigh, in a "Preliminary Notice" of his work on the relative densities of hydrogen and oxygen, of which advance sheets have been received while writing this note, that in our combustions the hydrogen may have been imperfectly burnt, especially as towards the last of the combustion it must have been greatly diluted (but with air). We have no decisive evidence on this point; but the whole course of our combustions assured us that this could not be the case. During the first stage of the combustion, when pure hydrogen was passing into the combustion tube, and while water was dropping into the condenser (Figure 4, page 163), there would often be several minutes — during which the larger part of the water was condensed — when no residual gas whatever would be seen to escape, and the bubbling of the gas through the sulphuric acid at the bend of the U tube made the least overflow perfectly evident. Again, the oxide of copper in the combustion tube was always reduced to a perfectly definite limit, leaving at least seven eighths of the tube in which the black oxide was apparently wholly unchanged. Further, it is not probable that an error arising from the imperfect combustion of the hydrogen would have a constant value. The unconsumed residue must vary greatly with the conditions of the experiment; and such an agreement as that exhibited by the results on page 173 could never have been obtained under such circumstances.

It seems unnecessary to add, that every precaution was taken in our work which our experience could suggest, and that a great amount of labor was spent on such details which does not appear in the published results. Both the balances and weights employed were most carefully verified. The water formed by the combustion was tested, and the dissolved air taken into account. We mention these points because they have been noticed by correspondents; but many similar details which were worked out and set one side we have not thought it necessary to describe in our paper. In writing such a paper elementary principles must be assumed.

In adopting Regnault's method for weighing the hydrogen used in our determinations, we assumed with him that the glass balloon used in the work remained practically constant, whether exhausted or filled with gas. We never questioned this assumption, not only because we had the greatest confidence in all Regnault's work, but also because we knew that he had himself carefully investigated the behavior of glass bulbs under pressure; and indeed he treats the subject fully in the paper immediately preceeding his classical paper on gas density.* Moreover, we made with our apparatus a preliminary determination of the density of air, and obtained Regnault's number within the limits of the uncertainty in regard to the value of the force of gravity at this place. Regnault's values for the weight of one litre, not only of air, but also of nitrogen, oxygen, hydrogen, and carbonic dioxide, have been hitherto regarded as among the most trustworthy data of science. His determinations were all made by the method of counterpoise which we adopted in our work, and he used balloons of twice the volume of those we employed. When exhausted, the glass must have been condensed to an even greater extent than has been shown above; but no account whatever is taken of this shrinkage. As Regnault's constants have been universally used, it is obvious that Lord Rayleigh's correction must be applied to all determinations of gas or vapor densities hitherto made, and to all atomic weight determinations of any kind which involve the calculation of the weight of a measured volume of any gas or vapor. Except, however, in the case of hydrogen, the correction will be inconsiderable.

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* Mémoires de l'Acad. Roy. des Sciences de l'Inst. de France, vol. xxi. pp. 106 and 121.

J. P. C. CAMBRIDGE, March 15, 1888.